

Reactivity of alkali and alkaline earth metal tetrafluorobromates towards aromatic compounds and pyridine



Vasily I. Sobolev^{a,*}, Victor D. Filimonov^b, Roman V. Ostvald^a, Vyacheslav B. Radchenko^b, Ivan I. Zherin^a

^a Department of Rare, Scattered and Radioactive Element Technology National Research Tomsk Polytechnic University, 634050 Tomsk, Russia

^b Department of Biotechnology and Organic Chemistry National Research Tomsk Polytechnic University, 634050 Tomsk, Russia

ARTICLE INFO

Article history:

Received 11 October 2016

Received in revised form 17 October 2016

Accepted 18 October 2016

Available online 2 November 2016

Keywords:

Bromine trifluoride
Tetrafluorobromates
Bromination
Fluorine
Arenes

ABSTRACT

The bromination activity of tetrafluorobromates of alkali and alkali-earth metals increases in the order KBrF_4 , CsBrF_4 , RbBrF_4 and $\text{Ba}(\text{BrF}_4)_2$. The most active tetrafluorobromate— $\text{Ba}(\text{BrF}_4)_2$ is able to selectively brominate the deactivated aromatic compounds nitrobenzene and 4-nitrotoluene, but not the activated compounds benzene and toluene. In all cases bromination of methyl groups of methylbenzenes does not occur. $\text{Ba}(\text{BrF}_4)_2$ forms the known complex $\text{C}_6\text{H}_5\text{N}\cdot\text{BrF}_3$ when reacted with pyridine. Due to dilution by inert BaF_2 , this pyridine-based complex is air stable and can be considered as safer and more convenient reagent in comparison with the original fluorobromates; it can selectively brominate benzene and toluene in contrast with tetrafluorobromates.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Bromine trifluoride and other bromine fluorides are compounds with high fluorinating or brominating ability [1,2]. Particularly Rozen and Lerman showed that BrF_3 can selectively brominate highly deactivated arenes in the presence of bromine; at the same time pure BrF_3 gives complex mixture of products in the cases of benzene and activated arenes [3]. Also BrF_3 is a highly toxic and dangerous compound, with extremely high reactivity [2], especially with organic compounds which lead to explosions. These properties have restrained widespread application of BrF_3 in synthetic chemistry and its usage requires special techniques.

Tetrafluorobromates of alkali and alkali-earth metals (TFB), with the common formula $\text{M}_x(\text{BrF}_4)_y$, can be considered as BrF_3 -based complexes which are safer and more convenient for use than BrF_3 [4–9]. However, there is no systematic data about the reactivity of TFB towards organic compounds. Recently it was shown that the air-stable complex $\text{BrF}_3\text{-KHF}$ could be used in the desulfurizing fluorination of benzylic sulfides and dithioacetals at room temperature in CH_2Cl_2 solution [6]. Nevertheless, the chemical properties of such compounds in organic reactions are not well-researched and the influence of the M^{n+} cation is not explored.

Herein we describe chemical properties of known fluorobromates: KBrF_4 , CsBrF_4 , RbBrF_4 [7,8] and the recently described $\text{Ba}(\text{BrF}_4)_2$ [9] in reactions with aromatic compounds and pyridine.

2. Results and discussion

2.1. Reactions between KBrF_4 , CsBrF_4 , RbBrF_4 and $\text{Ba}(\text{BrF}_4)_2$ with nitrobenzene and 4-nitrotoluene

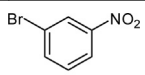
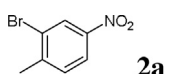

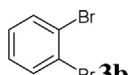
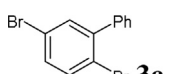

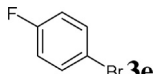
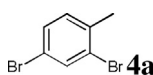
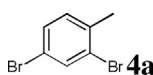
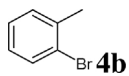
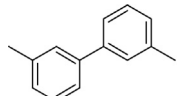
Initially the examined TFBs caused strong explosions and decomposition of the initially pure and dry organic substrates to unidentifiable mixtures. However, mild and selective conditions were found in the cases of nitrobenzene **1** and 4-nitrotoluene **2** to give the corresponding *m*-bromonitroarenes **1a** and **2a** with good yields. Addition of TFBs to substrates **1**, **2** in dry $\text{ClF}_2\text{CCl}_2\text{F}$ (Freon R113) was performed at -25°C with strong stirring before the cooling bath was removed. The reaction mass was stirred at 45°C for 5 h; the gradual gas evolution was observed. The absence of F_2 in the gaseous products was determined by a qualitative test with potassium iodide [10]. Analysis of the reaction mixture was performed using GC-MS and it was found that there were no fluorine-containing organic products.

Preparative yields of **1a** and **2a** (Table 1) in cases of different fluorobromates showed the reactivity order $\text{KBrF}_4 < \text{RbBrF}_4 < \text{CsBrF}_4 \ll \text{Ba}(\text{BrF}_4)_2$. It was also found that strongly deactivated 1,3-dinitrobenzene is inert to $\text{Ba}(\text{BrF}_4)_2$.

* Corresponding author.

E-mail address: vsobolev1989@tpu.ru (V.I. Sobolev).

Table 1
Reactions of KBrF₄, CsBrF₄, RbBrF₄ and Ba(BrF₄)₂ with arenes **1–4**.^a

Substrate	Reagent	Product	Yield (%)
Nitrobenzene 1	KBrF ₄		12 ^b
	RbBrF ₄		14 ^b
	CsBrF ₄		24 ^b
	Ba(BrF ₄) ₂		84 ^b
4-Nitrotoluene 2	Ba(BrF ₄) ₂		87 ^b
Benzene 3	Ba(BrF ₄) ₂		16 ^c
			34 ^c
			17 ^c
			12 ^c
			8 ^c
Toluene 4	Ba(BrF ₄) ₂		24 ^c
			14 ^c
			17 ^c
			9 ^c

^a Representative procedure: arenes (4 mmol), TFB (2 mmol), Freon R 113 (4.1 mL).^b Isolated yields.^c GC.

2.2. Reactions of Ba(BrF₄)₂ with benzene and toluene

At the same time benzene **3** and toluene **4** reacted unselectively with Ba(BrF₄)₂ under the described conditions to give inseparable mixture. In these cases in according to GC data, the main products were bromoarenes **3a, b** and **4a, b** with various biphenyls **3c, d** and **4c** and traces of bromo-fluoro arenes **3e** and **4d** were also identified. The formation of biphenyls **3c, d** and **4c** shows that Ba(BrF₄)₂ also possesses oxidation ability towards non-deactivated arenes. It is important to note that no products of methyl group

benzylic bromination with methylarenes **2, 4** was observed which shows that the mechanism is electrophilic rather than free-radical.

2.3. Reaction of Ba(BrF₄)₂ with pyridine

It is well-known that pyridine **5** has low reactivity in electrophilic bromination processes [11]. In the reaction of pyridine **5** with Ba(BrF₄)₂ we observed the exothermic (temperature increase to 40 °C) decomposition of Ba(BrF₄)₂ to BaF₂. No pyridine or pyridine-based compounds were observed in the liquid phase, but the solid phase contained a pyridine derivative with high reactivity. This solid phase product rapidly exploded upon the addition of water with the formation of bromine, hydrogen fluoride and pyridine. It is known that the C₆H₅N·BrF₃ complex **6** can be obtained from the reaction of pyridine and BrF₃ [12,13]. Therefore it is proposed that the C₆H₅N·BrF₃ complex diluted by BaF₂ was formed in the explored reaction (Fig. 1).

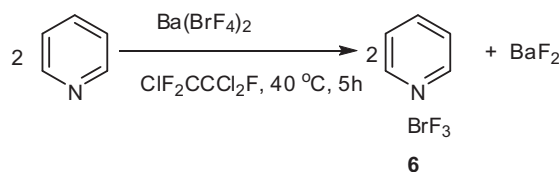
The pure C₆H₅N·BrF₃ complex was unstable and rapidly decomposed in air and upon contact with water, however its lifetime in CHCl₃, CCl₄ suspensions was about 8–10 h. The high reactivity of **6** did not allow acquisition of liquid or solid state NMR spectra of this compound [13,14].

Dilution of complex **6** by BaF₂ (Fig. 1) lowers its reactivity and makes it easier to handle. The diluted complex can be stored in dry air indefinitely. In contrast to Ba(BrF₄)₂ it does not react explosively with organic compounds. At the same time complex **6**-BaF₂ has sufficient reactivity and unlikely to BrF₃ and Ba(BrF₄)₂ can selectively brominate not only the deactivated arenes nitrobenzene **1** and 4-nitrotoluene **2**, but even the activated arenes benzene **3** and toluene **4** (Table 2).

These experiments showed that **6**-BaF₂ is a milder brominating reagent than BrF₃ and even Ba(BrF₄)₂. It is important to note no benzylic bromination and fluorine-containing products were formed. It is also interesting that the reaction of **6**-BaF₂ and toluene **4** has unusually high *ortho*-selectivity, which leads to the formation of *o*-bromotoluene **4b** as a single isomer. Such high *ortho*-selectivity is rare in the bromination of toluene. Usually there is high *para*-selectivity [11], while *ortho*-selective bromination can be achieved using N-bromosuccinimide in the presence of NaHCO₃·SiO₂ with toluene **4** in 20% conversion only [15].

The mechanism of the observed TFB brominating activity is unclear and requires further research. The reaction between arenes and insoluble TFB causes its decomposition; this means that reaction starts from the formation of some complexes probably Mδ⁻δ⁺BrF₃-Ar on the surface of TFB. We can also propose that their decomposition leads to the formation of hypervalent bromine aromatic intermediates, aryl-difluoro-λ³-bromanes (ArBrF₂) [16], which after the reaction mass quench by H₂O, NaNO₂ and CaCl₂ (see experimental procedure) give the corresponding aryl bromides. The proposed hypothesis at least provides an explanation of the observed electrophilic type of bromination.

It is also possible to consider an alternative reaction based on the formation of Br₂ and F₂ (with following *in situ* formation of bromine fluorides) upon the decomposition of TFB by arenes. However, this idea contradicts the absence of F₂ in the gaseous

**Fig. 1.** Formation scheme of C₆H₅N·BrF₃ complex **6** diluted by BaF₂.

Download English Version:

<https://daneshyari.com/en/article/5152177>

Download Persian Version:

<https://daneshyari.com/article/5152177>

[Daneshyari.com](https://daneshyari.com)